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**Chutjian et al.**

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(54) **MINIATURE MICROMACHINED  
QUADRUPOLE MASS SPECTROMETER  
ARRAY AND METHOD OF MAKING THE  
SAME**

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### Related U.S. Application Data

(62) Division of application No. 09/305,807, filed on Apr. 28, 1999, now Pat. No. 6,049,052, which is a continuation of application No. 09/089,781, filed on Jun. 3, 1998, now abandoned.

(60) Provisional application No. 60/048,540, filed on Jun. 3, 1997.

(51) **Int. Cl.**<sup>7</sup> ..... **H01J 49/42**

(52) **U.S. Cl.** ..... **250/292; 250/396 R**

(58) **Field of Search** ..... 250/292, 396 R;  
219/69.12, 69.17

(56) **References Cited**

## U.S. PATENT DOCUMENTS

2,939,952	*	1960	Paul et al. ....	250/292
5,248,883		9/1993	Brewer et al. ....	250/292
5,596,193	*	1/1997	Chutjian et al. ....	250/292
5,719,393		2/1998	Chutjian et al. ....	250/292
5,852,270		12/1998	Holkeboer ....	219/69.12
6,049,052		4/2000	Chutjian et al. ....	250/292

\* cited by examiner

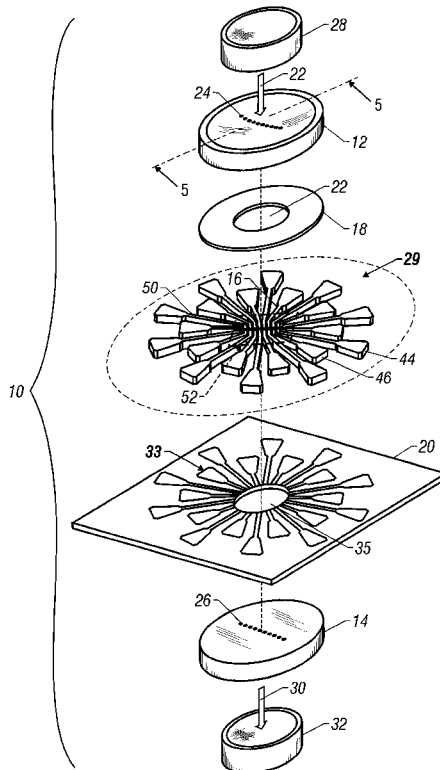
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(57) **ABSTRACT**

The present invention provides a quadrupole mass spectrometer and an ion filter, or pole array, for use in the quadrupole mass spectrometer. The ion filter includes a three patterned layer including a two-dimensional array of poles forming one or more quadrupoles. The patterned layer design permits the use of very short poles and with a very dense spacing of the poles, so that the ion filter may be made very small. Also provided is a method for making the ion filter and the quadrupole mass spectrometer. The method involves forming the patterned layer of the ion filter in such a way that as the poles of the patterned layer are formed, they have the relative positioning and alignment for use in a final quadrupole mass spectrometer device.

**20 Claims, 5 Drawing Sheets**



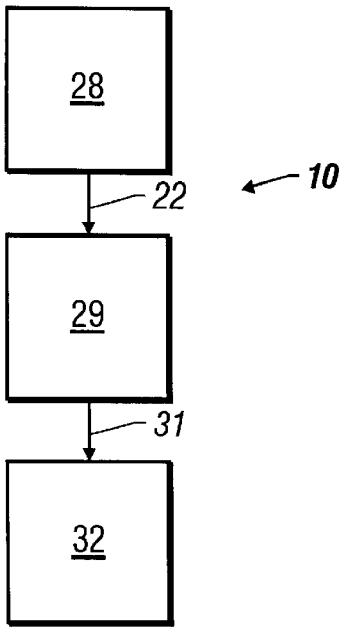


FIG. 1

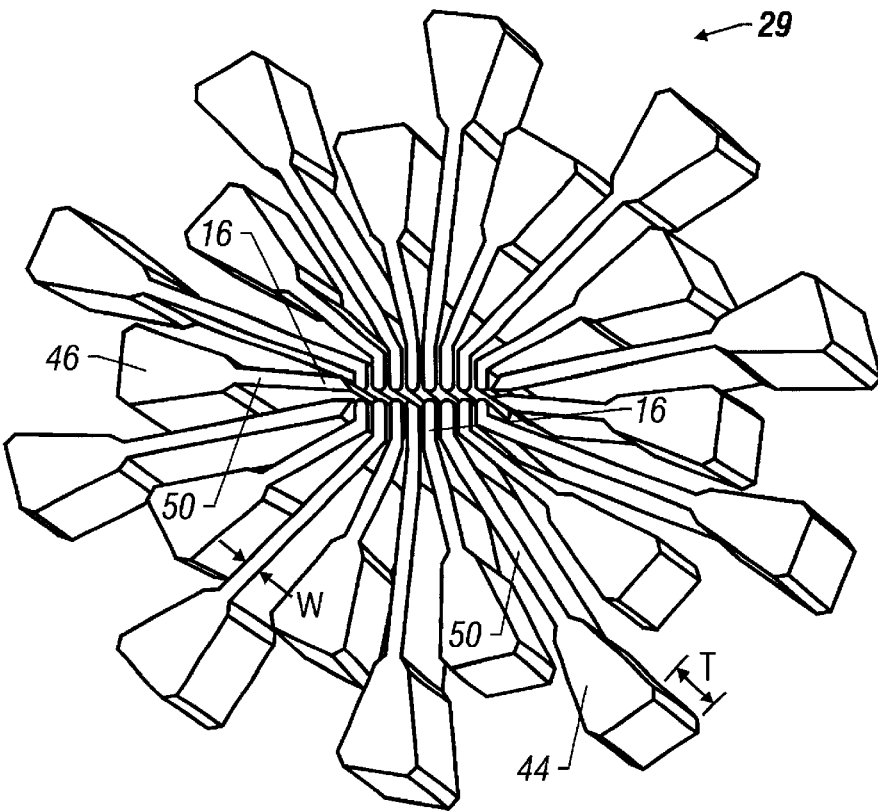


FIG. 3

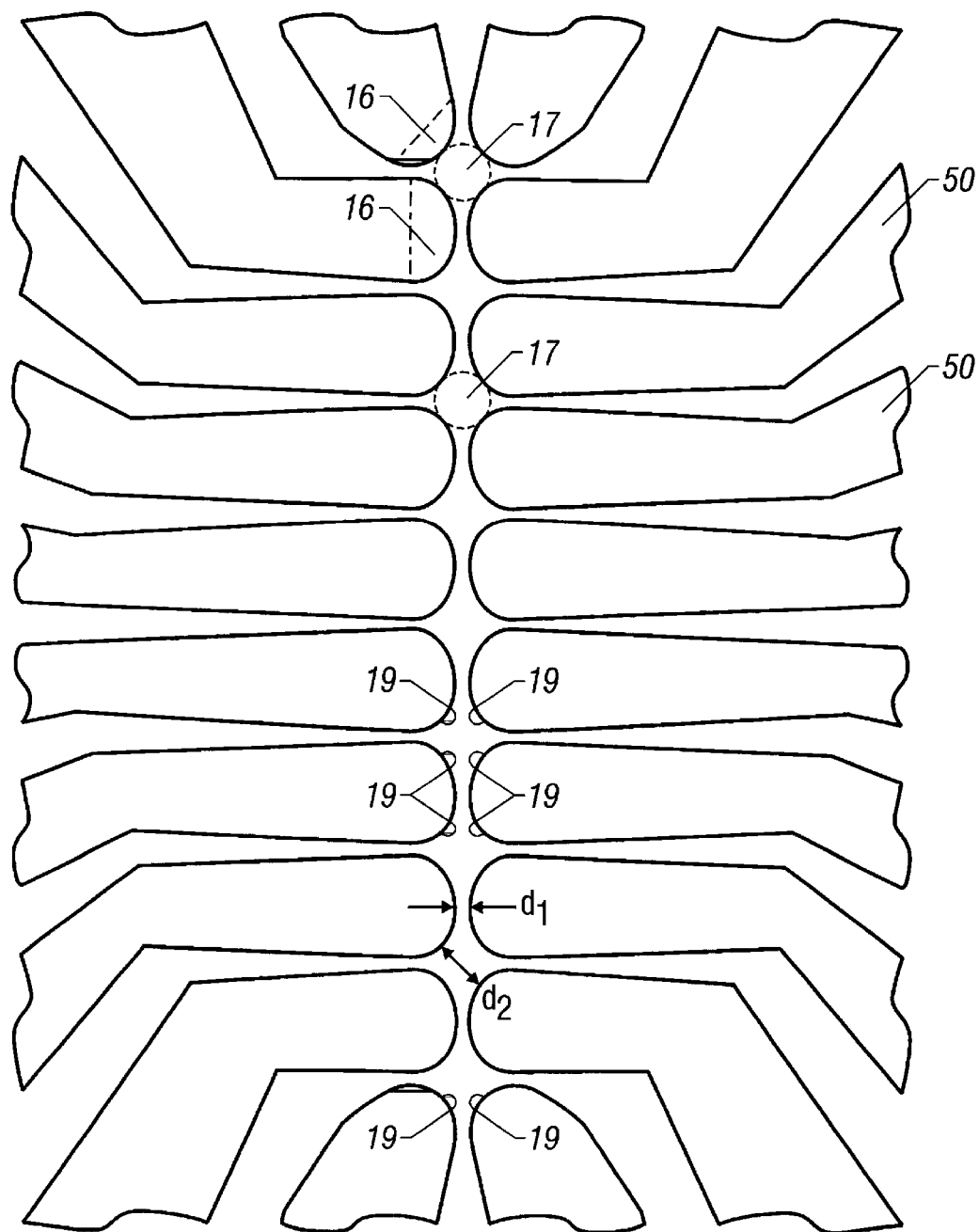


FIG. 2

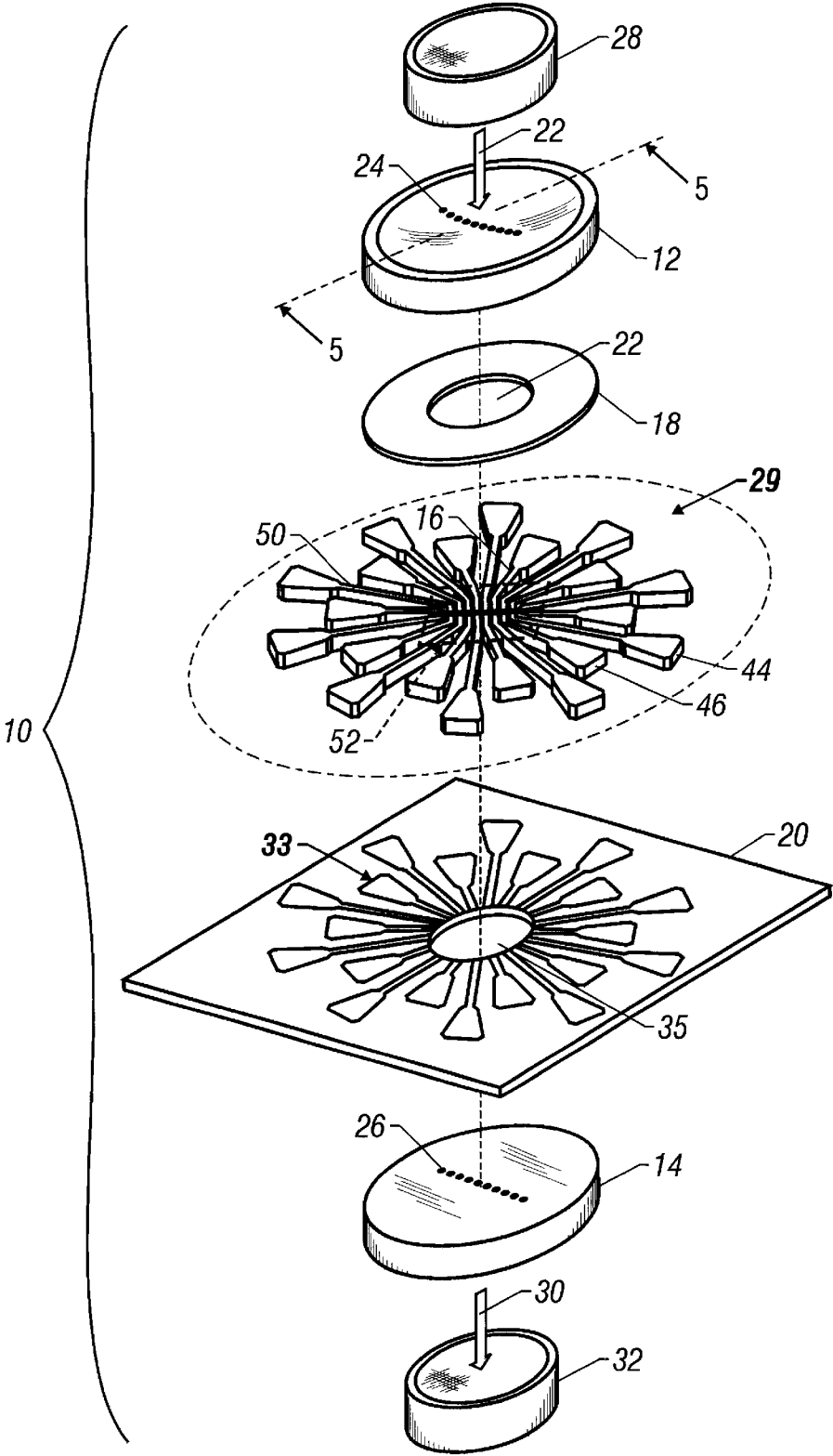


FIG. 4

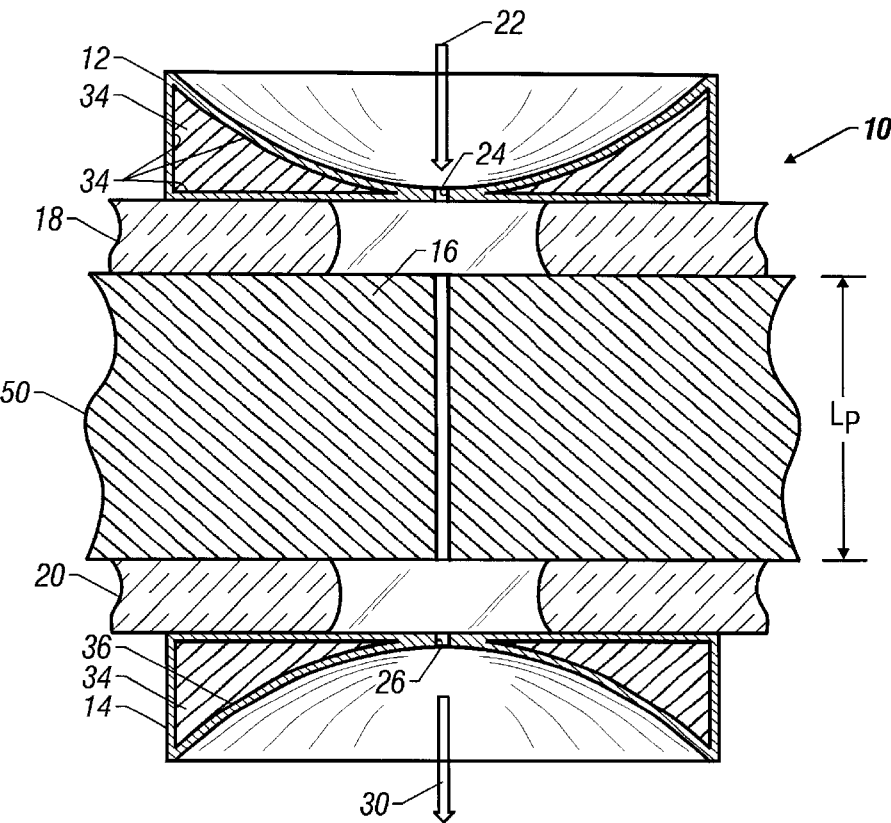


FIG. 5

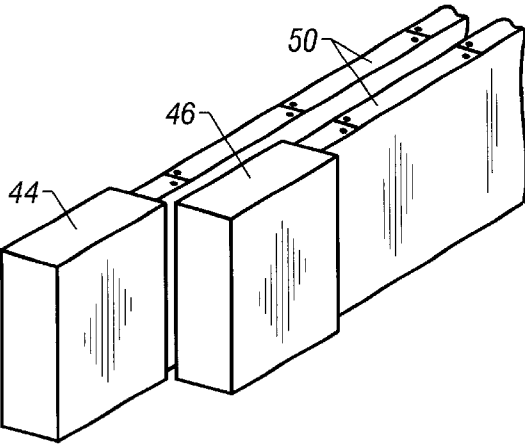


FIG. 6

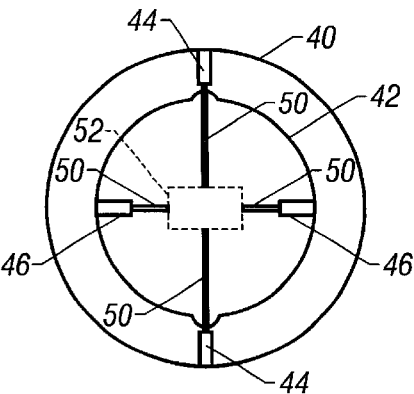
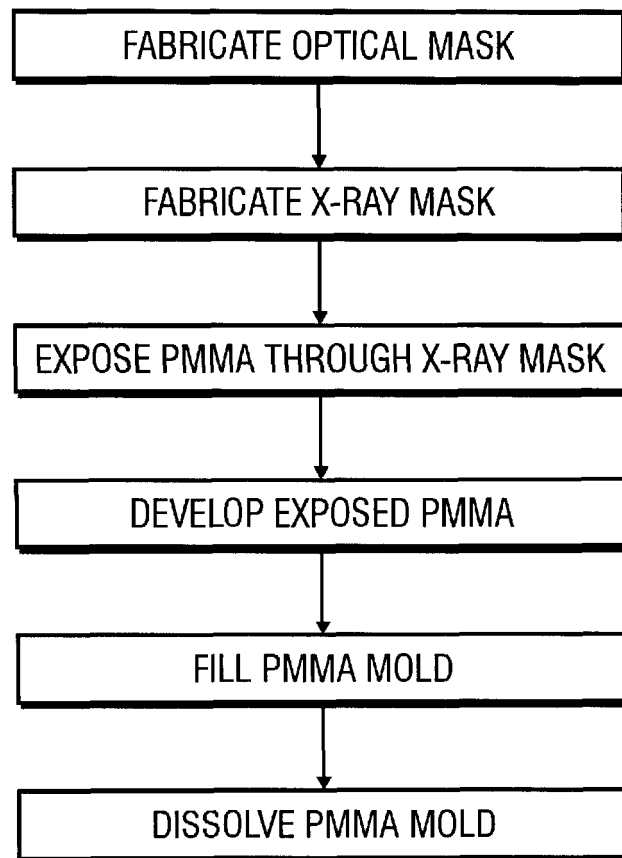
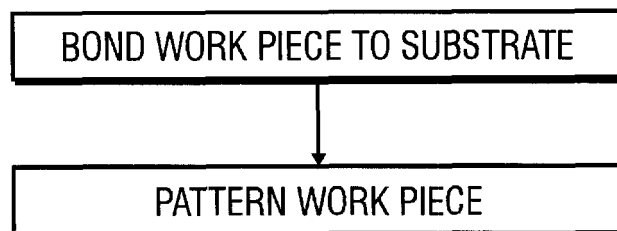


FIG. 7

**FIG. 8****FIG. 9**

# MINIATURE MICROMACHINED QUADRUPOLE MASS SPECTROMETER ARRAY AND METHOD OF MAKING THE SAME

## CROSS-REFERENCE TO RELATED APPLICATIONS

This is a divisional of U.S. application Ser. No. 09/305, 807, filed Apr. 28, 1999, now U.S. Pat. No. 6,049,052, which is a continuation of U.S. application Ser. No. 09/089,781, filed Jun. 3, 1998, now abandoned.

This application claims the benefit of priority under 35 U.S.C. § 119 to U.S. Provisional Patent Application No. 60/048,540, filed Jun. 3, 1997. The entire contents of U.S. Provisional Patent Application No. 60/048,540 are incorporated herein, as if set forth herein in full.

## ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

## FIELD OF THE INVENTION

The present invention generally relates to quadrupole mass spectrometers. In particular, the present invention relates to a miniature micromachined ion filter for use in a quadrupole mass spectrometer, a quadrupole mass spectrometer including the ion filter, and methods of making the ion filter and the a quadrupole mass spectrometer.

## BACKGROUND OF THE INVENTION

Mass spectrometers are workhorse instruments finding applications in many commercial and military markets, with potential for use in domestic markets as well. A mass spectrometer is able to sample, in situ, the atmosphere in which it is placed and provide a reading of the atomic and molecular species (and any positive or negative ions) present in that atmosphere and of the absolute abundance of these species.

There are many types of mass spectrometers, such as magnetic sector, Paul or Penning ion trap, trochoidal monochromator, and the like. One popular type of mass spectrometer is the quadrupole mass spectrometer (QMS), first proposed by W. Paul (1958). In general, the QMS separates ions with different masses by applying a direct current voltage and a radio frequency ("RF") voltage on four rods having hyperbolic or circular cross sections and an axis equidistant from each rod. Opposite rods have identical potentials. The electric potential in the quadrupole is a quadratic function of the coordinates.

Ions are introduced in a longitudinal direction through a circular entrance aperture located at the ends of the rods and centered on the midpoints between rods. Ions are deflected by the field depending on their atomic mass-to-charge ( $m/z$ ) ratio. By selecting the applied voltage amplitude and frequency of the RF signal, only ions of a selected  $m/z$  ratio exit the QMS along the axis of a quadrupole at the opposite end and are detected. Ions having other  $m/z$  ratios either impact the rods and are neutralized or deflect away from the centerline axis of the quadrupoles.

As explained in Boumsellek, et al. (1993), a solution of Mathieu's differential equations of motion in the case of round rods provides that to select ions with a  $m/z$  ratio using

an RF signal of frequency  $f$  and rods separated by a contained circle of radius distance  $R_0$  the peak RF voltage  $V_0$  and DC voltage  $U_0$  should be as follows:

$$\begin{aligned} V_0 &= 7.233 \text{ mV}^2 R_0^2 \\ U_0 &= 1.213 \text{ mV}^2 R_0^2 \end{aligned}$$

Conventional QMS's weigh several kilograms, have volumes of the order of  $10^4 \text{ cm}^3$ , and require 50–100 watts of power. Further, these devices usually operate at vacua in the range of  $10^{-6}$ – $10^{-8}$  torr in order that the mean free path be comparable to the instrument dimensions, and where secondary ion-molecule collisions cannot occur. Commercial QMS's of this design have been used for characterizing trace components in the atmosphere (environmental monitoring), automobile exhausts, chemical-vapor deposition, plasma processing, and explosives/controlled-substances detection (forensic applications). However, such conventional QMS's are not suitable for spacecraft life-support systems and certain national defense missions where they have the disadvantages of relatively large mass, volume, and power requirements. A small, low-power QMS would find a myriad of applications in factory air-quality monitoring, pollution detection in homes and cars, protection of military sites, and protection of public buildings and transportation systems (e.g., airports, subways, and harbors) against terrorist activities.

One type of miniature QMS (U.S. Pat. No. 5,401,962) was developed by Ferran Scientific, Inc., San Diego, Calif. and includes a miniature array of sixteen rods comprising nine individual quadrupoles. The rods are supported only at the detector end of the QMS by means of powdered glass that is heated and cooled to form a solid support structure. The electric potential and RF voltage are applied by the use of springs contacting the rods. The Ferran QMS dimensions are approximately 2 cm diameter by 5 cm long, including a gas ionizer and detector, and has an estimated mass of 50 grams. The reduced size of the Ferran QMS results in several advantages over existing QMS's, including a reduced power consumption and a higher operating pressure.

The Ferran QMS has a resolution of approximately 1.5 amu in the mass range 1–95 amu. This is a relatively low resolution for a QMS, making the miniature Ferran QMS useful for commercial processing (e.g., chemical-vapor deposition, blood-plasma monitoring) but not for applications that require accurate mass separation, such as in analytical chemistry and in spacecraft life-support systems. Boumsellek et al. (1993) traced the low resolution to the fact that the rods were aligned only to within a  $\pm 3\%$  accuracy, whereas an alignment accuracy in the range of  $\pm 0.1\%$  is necessary for a high resolution QMS.

A separate miniature QMS (U.S. Pat. Nos. 5,596,193 and 5,719,393) was developed by the Jet Propulsion Laboratory (JPL), California Institute of Technology to address the continuing need for a reduced size QMS having an acceptable rod alignment. The JPL QMS provides improved resolution over the Ferran QMS due to improved accuracy in rod alignment. As may be appreciate, the accurate positioning and alignment of individual miniature rods in an array significantly increases the cost of manufacturing due to the increased time and specialized equipment required for precisely aligning separated miniature rods. As the size of the rods is further reduced, the complexity, difficulty and expense of rod positioning and alignment increases. In this regard, there is a need for a small QMS having high resolution that may be made by simpler and less expensive manufacturing process.

## SUMMARY OF THE INVENTION

In one aspect, the present invention provides a quadrupole ion filter, and a quadrupole mass spectrometer including the ion filter, that avoids problems associated with miniaturization of conventional quadrupole mass spectrometer devices, and especially problems concerning the incorporation of loose rods into conventional devices. The ion filter includes a patterned layer of electrically conductive material, with the patterned layer including a two-dimensional array of poles for one or more quadrupoles. Alternatively, the ion filter may be described as a pole array. The pole array, or array of poles, in the pattern is two-dimensional in that the poles in the array have a regular spacing in the x-y plane, with the length of the poles in the array being in the z direction. The poles of the ion filter serve the same function as the rods in conventional quadrupole devices. The patterned layer is divided into a number of separate sections, or pieces, each including at one terminal end one pole in the array of poles. At the other terminal end of each separate piece is a bonding location for convenient electrical connection of the piece with an external power source.

Structurally, the quadrupole ion filter of the present invention is considerably different than the quadrupole structure in conventional quadrupole mass spectrometers. Conventional quadrupole mass spectrometers, even those that have been minimized, use poles that are in the form of individual longitudinally extending rods. The ion filter of the present invention, however, includes the array of poles in a thin patterned layer, with the thickness of the layer corresponding with the length of the poles.

The patterned layer in the ion filter of the present invention typically has a thickness of smaller than about 6 millimeters, although even smaller thicknesses may be preferred for some applications. In that regard, the thinner that the patterned layer is, the shorter the length of poles and, therefore, the shorter the distance that ions must travel to pass through the ion filter. A shorter length of travel through the ion filter permits operation at higher pressures, which is a significant advantage with the ion filter of the present invention.

By use of the patterned layer in the ion filter of the present invention, it is possible to make the poles of an extremely small size and with an extremely dense spacing. For example, with the present invention, the density of poles in the patterned layer is typically greater than about 2 poles per square millimeter, and in many embodiments the density is much higher. Furthermore, directly opposing poles in the patterned layer are typically separated by a distance of shorter than about 0.2 millimeter, and in many embodiments by an even shorter distance. Diagonally opposing poles in the patterned layer are typically separated by a distance shorter than about 0.3 millimeter, and in many embodiments by an even shorter distance. Because of the extremely small size and dense spacing of the poles, the ion filter may include a large array of poles in a small space, with different groupings of four adjacent poles each defining a channel for passage of ions. With the present invention, however, these quadrupole channels are extremely small. When the ion filter includes a large array of poles, defining a plurality of quadrupole channels, the channels are typically present in a density of larger than about one of the quadrupole channels per square millimeter, and often greater than two of the quadrupole channels per square millimeter.

An advantageous structure for the ion filter of the present invention is one in which substantially all of the patterned layer is supported by a single, common supporting substrate,

which is typically of dielectric material. The patterned layer is such, however, that a portion of the patterned layer that includes the poles is suspended from the substrate. Typically, the suspended portion of the patterned layer extends over an opening that passes through the substrate. In this way, the opening provides a passageway to permit ions access to the quadrupole channels. The patterned layer is bonded to the supporting substrate in a manner that maintains positioning and alignment of the poles, even though the poles are suspended from the substrate.

A significant aspect of the present invention is manufacture of the quadrupole ion filter, and manufacture of quadrupole mass spectrometers including the ion filter. According to the present invention, a method is provided in which the poles in the patterned layer are made in a manner such that as the poles are made they have relative positioning and alignment for final use in a quadrupole mass spectrometer. This is typically accomplished, according to the method of the present invention, by forming the patterned layer of the ion filter on a common supporting substrate so that the patterned layer, as formed on the common supporting substrate, is bound to the substrate, such that the relative positioning and alignment of poles in the patterned layer is thereby fixed.

One preferred embodiment of the method for manufacturing the ion filter involves simultaneous manufacture of the patterned layer, including the poles, by filling a mold with electrically conductive material. The mold includes a template for the patterned layer. The mold is filled when it is situated on the surface of the common supporting substrate. When the mold is then removed, the patterned layer remains supported by the common supporting substrate. In one embodiment, the mold may be made by a technique known as Lithographic-Galvanoformung-Abformung (LIGA) manufacture.

Another embodiment of the method for manufacturing the present invention involves forming the patterned layer from a single work piece, typically in the form of a metallic sheet, that has been bonded to the common supporting substrate. Material is selectively removed from the work piece to form the patterned layer, such that the patterned layer, as formed, is bound to and supported by the common supporting substrate. Typically, the selective removal of material from the work piece is accomplished by electrical discharge machining (EDM).

The present invention also involves a quadrupole mass spectrometer including the mass filter of the present invention. The quadrupole mass spectrometer includes the ion filter located between an ion source and an ion detector. During operation, the ion source supplies ions to be filtered by the ion filter. Ions passing through the ion filter may then be detected by the ion detector. The quadrupole mass spectrometer may include spacers before and/or after the ion filter to maintain a predetermined spacing between the ion filter and the ion source and/or the ion detector and to assist in isolating the operation of the ion filter from influences from other components. These spacers are typically made of dielectric material. The quadrupole mass spectrometer may also include entrance and/or exit devices for enhancing performance of the quadrupole mass spectrometer. The entrance device is located between the ion source and the ion filter and typically includes a body of dielectric material having apertures therethrough for channeling ions from the ion source into the ion filter. In a preferred embodiment, the entrance device includes an electrically conductive metallic film at least on a side facing the ion source, to dissipate the charge of ions striking the entrance device. The exit device



similarly includes a body of dielectric material having apertures therethrough for channeling ions exiting the mass filter to the ion detector. In a preferred embodiment, the exit device includes an electrically conductive metallic film on at least a side facing the ion filter, to dissipate the charge of ions striking the exit device.

Furthermore, the quadrupole mass spectrometer has a versatile design that may be adapted to a variety of situations. For example, a Faraday-type ion detector may be used for operation at relatively high pressures, often in the millitorr range. For operation of the device at very low pressures, such as those below about  $10^{-4}$  torr, a single particle multiplier may be used as the ion detector.

Also, according to the present invention, the quadrupole mass spectrometer including the ion filter may easily be manufactured through proper alignment and assemblage of the individual components.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing major components of one embodiment of a quadrupole mass spectrometer of the present invention;

FIG. 2 is a partial top view, drawn to a large scale, of one embodiment of an array of poles in an ion filter of the present invention;

FIG. 3 is a perspective view of one embodiment of an ion filter of the present invention;

FIG. 4 is an exploded view in perspective illustrating several of the components and their arrangement in one embodiment of a quadrupole mass spectrometer of the present invention;

FIG. 5 is a partial cross section through a single pair of metallic poles of one embodiment of a quadrupole mass spectrometer array of the present invention;

FIG. 6 is a partial perspective view of a bonding pad configuration with connecting strips attached to alternate poles of one embodiment of a quadrupole mass spectrometer of the present invention;

FIG. 7 is a top view of one embodiment of a bonding configuration for making electrical connection to poles of an ion filter of the present invention;

FIG. 8 is a flow diagram illustrating one embodiment of a LIGA-based process of the present invention for making an ion filter for use in a quadrupole mass spectrometer;

FIG. 9 is a flow diagram illustrating one embodiment of an EDM-based process of the present invention for making an ion filter for use in a quadrupole mass spectrometer.

DETAILED DESCRIPTION

The present invention provides a quadrupole mass spectrometer comprising an ion source, an ion filter, and an ion detector, useful for in situ sampling of an atmosphere for identification of atomic and molecular species that may be present in the atmosphere. The present invention also includes an ion filter for use in the quadrupole mass spectrometer including an array of at least 4 miniature poles defining at least one quadrupole channel through which ions pass for detection. The ion filter can may also be desired as a pole array. The pole array, or array of poles is typically used to perform the ion filtering function in the mass filter composed of the quadrupole mass spectrometer. The ion filter typically comprise a sufficiently large two-dimensional array of poles to define a plurality of quadrupole channels in a quadrupole mass spectrometer array (QMSA). Having a

plurality of quadrupole channels is advantageous to enhance detection sensitivity, especially for the miniature device of the present invention because the detection sensitivity associated with a quadrupole channel generally decreases with decreasing channel size, due to the smaller cross-sectional area of the channel that is available for passage of ions.

Referring now to FIG. 1 the major components of the quadrupole mass spectrometer of the present invention are shown. As illustrated in FIG. 1, a miniature micromachined quadrupole mass spectrometer 10 is shown including an ion source 28, an ion filter 29, and an ion detector 32. The mass spectrometer 10 operates according to known principles. During operation, the ion source 28 provides ions in an ion beam 22. Ions in the ion beam 22 travel to the ion filter 29 where ions are filtered according to the  $m/z$  ratio of the ions, with  $m$  referring to the mass of an ion and  $z$  referring to the charge of an ion. Mass filtered ions 31 exiting the ion filter 29 may then be detected by the ion detector 32. At any given time, the mass filtered ions 31 include substantially only ions in a narrow range of  $m/z$  ratios, so that the ion detector 32, at any given time, is detecting only ions within the narrow range. The location of the  $m/z$  range of the mass filtered ions 31 may be periodically or continuously varied by varying RF frequency and voltages to the ion filter 29, as discussed further below, using control electronics known in the art. In this way, the mass spectrometer may be used to detect ions over a wide range of  $m/z$  values. Information from the ion detector 32 concerning detected ions may be interpreted by techniques known in the art for identification of atomic and molecular species originally present in the atmosphere being sampled by the mass spectrometer 10.

The ion source 28 may be any apparatus capable of generating ions for filtering in the ion filter 29. Examples of the ion source 28 include a field-emission ionizer and an electron-impact ionizer. Preferred as the ion source 28 is an electron-impact ionizer.

The ion detector may be any apparatus capable of detecting the mass filtered ions 31. Examples of the ion detector 32 include a Faraday-type ion detector, a single-particle multiplier and a flat micromachined plate. Preferred as the ion detector 32 is a miniature micromachined-plate ion multiplier.

The ion filter 29 includes the QMSA of the present invention as an active element for filtering ions for detection. The QMSA filters ions based on general principles well known in the operation of quadrupole mass spectrometers. The QMSA of the present invention, however, can be of an extremely small size, which is advantageous for many uses, especially when size or weight considerations are important, such as in space applications. Also, the QMSA of the present invention is manufacturable by micromachining techniques that lend themselves to relatively high volume, low cost manufacture.

One embodiment of the QMSA of the present invention is shown in FIG. 2, including an array of poles 16, with any grouping of four adjacent poles 16 defining a quadrupole channel 17 through which ions travel during use. The quadrupole channel 17 refers to the space defined by any grouping of four poles 16 within areal boundaries defined by a circle that is substantially tangent to each of the four relevant poles 16, as exemplified by the dotted circles shown for two of the quadrupole channels 17 in FIG. 2. Each of the poles 16 form an integral structure with a connecting strip 50, which acts as an electrical lead to the respective one of the poles 16. Each of the poles 16, therefore, forms the terminal portion of an integral piece including one of the poles 16 and a corresponding connecting strip 50.

With continued reference to FIG. 2, each of the poles 16 has either one or two curved exterior surfaces 19, such that each of the quadrupole channels 17 has four of the curved surfaces 19 facing the quadrupole channel 17. The curved surfaces 19 as shown in FIG. 2 have a hyperbolic shape, which is preferred for the poles 16. Other surface shapes, could, however, be used, such as an arc of a circle.

In a conventional quadrupole mass spectrometer, the poles would be separate pieces, such as individual circular rods, assembled in an array. With reference to FIG. 2, the poles 16 of the QMSA of the present invention are significantly different than the poles in conventional quadrupole mass spectrometers, because the poles 16 are a terminal portion of a larger integral structure, as noted above. The terminal portions forming the poles 16 of the present invention generally include only the terminal portions of the integral structure generally within the area defined by the curved surfaces 19, as shown by the dotted lines shown for two of the poles 16 in FIG. 2. One significant advantage of the poles 16 of the present invention is their small size. Typically, the cross sectional area of the poles 16 (i.e., the terminal area inside of the dotted lines shown in FIG. 2) is smaller than about 0.3 square millimeter, preferably smaller than about 0.2 square millimeter and more preferably smaller than about 0.1 square millimeter.

A significant advantage of the QMSA of the present invention is the extremely small size and dense spacing of the poles 16 forming the array. With continued reference to FIG. 2, in a preferred embodiment, the face-to-face spacing (d1) between adjacent, directly opposing poles 16 is smaller than about 0.2 millimeter, preferably smaller than about 0.15 millimeter, and most preferably smaller than about 0.1 millimeter. Spacing (d2) between diagonally opposing poles 16 is preferably smaller than about 0.3 millimeter, more preferably smaller than about 0.25 millimeter, still more preferably smaller than about 0.2 millimeter and most preferably smaller than about 0.15 millimeter. According to the present invention, the density of quadrupoles in the QMSA is typically greater than about 2 quadrupoles per square millimeter, preferably greater than about 3 quadrupoles per square millimeter, more preferably greater than about 4 quadrupoles per square millimeter, and most preferably greater than about 5 quadrupoles per square millimeter, with the area measured in a plane perpendicular to the longitudinal axes of the quadrupoles in the array. As used herein, a quadrupole refers to the equipotential area, when the device is operating, in the area of a quadrupole channel 17 defined by any grouping of four adjacent of the poles 16 of the array. With such a high density of quadrupoles per cross-sectional area, the QMSA can easily accommodate 10 quadrupoles in devices designed for applications having even the tightest space requirements, and more preferably at least 100 quadrupoles. The density of poles 16 in the array is preferably greater than about 2 poles per square millimeter, more preferably greater than 4 poles 16 per square millimeter, still more preferably greater than about 6 poles 16 per square millimeter, and most preferably greater than about 8 poles 16 per square millimeter. Particularly preferred is a pole density in the array of greater than about 10 poles 16 per square millimeter. With the dense spacing of the adjacently located poles 16 and, thus, dense spacing of quadrupoles, the spacing density of the quadrupole channels 17 is typically one or more of the quadrupole channels 17 per square millimeter, and preferably more than about two of the quadrupole channels 17 per square millimeter. When the array of the poles 16 defines more than one quadrupole and, consequently more than one of the quadrupole channels 17,

the number of poles 16 will be at least 6, and preferably at least 20 and more preferably at least 100. Furthermore, the area of each of the quadrupole channels 17 for accepting ions (i.e., the area of the exemplified inscribed circles in FIG. 2) is very small, typically smaller than about 0.05 square millimeter, preferably smaller than about 0.03 square millimeter and more preferably smaller than about 0.02 square millimeter.

The poles 16 of the array are positioned between the ion source 28 and the ion detector 32 of the quadrupole mass spectrometer such that substantially the entire length of each pole 16 is within the space between the ion source and the ion detector. The poles 16 preferably have a length of shorter than about 6 millimeters, more preferably a length of shorter than about 4 millimeters, even more preferably a length of shorter than about 3 millimeters. In one embodiment, the length of the poles 16 is shorter than about 2 millimeters.

The QMSA is part of the ion filter 29 of the present invention. One embodiment of the ion filter 29 is shown in FIG. 3. The ion filter 29 includes a thin patterned layer of electrically conductive material, preferably of an electrically conductive metal such as gold or titanium. The patterned layer includes a plurality of elongated electrically conducting portions, each including a single integral piece a pole 16, a bonding pad 44 or 46, and a connecting strip 50, with the connecting strip 50 being located intermediate between the pole 16 and the bonding pad 44 or 46.

The pole 16 is located at one terminal end of each integral piece, as previously described with reference to FIG. 2, and the bonding pad 44 or 46 is located at the opposite terminal end. The bonding pad 44 or 46 provides a location for making an electrical connection to an external power source for providing power to the array of the poles 16, and the connecting strip 50 provides an electrical lead from the bonding pad 44 or 46 to the pole 16. As shown, the bonding pad 44 or 46 has a greater width than the pole 16 or the connecting strip 50. Although not necessary to the present invention, having a wider area available for bonding is preferred for ease of making an electrical connection. Preferably, the bonding pad 44 or 46 is suitable for making a wire bond connection to an external power source.

Preferably, each of the integral pieces has a substantially constant layer thickness (shown as dimension T in FIG. 3) for all of the bonding pad 44 or 46, connecting strip 50 and pole 16. Furthermore, it is preferred that all of the integral pieces making up the patterned layer are of substantially the same thickness. A substantially constant thickness for the patterned layer facilitates ease of manufacture of the ion filter 29 and incorporation of the ion filter 29 into a quadrupole mass spectrometer. The thickness of the patterned layer is preferably substantially equal to the length of the poles 16. The connecting strips 50 preferably have a width (shown as dimension W in FIG. 3) of smaller than about 0.5 millimeter.

The patterned layer of the ion filter 29 is typically substantially all supported by a common substrate. This is important both from a manufacturing perspective, as discussed below, and from an operational perspective, due to the narrow tolerances achievable when the integral pieces for all of the poles 16 are supported by a common substrate. The common substrate is typically of a dielectric material. Examples of such dielectric materials include alumina and glass. Furthermore, the common substrate will typically include an opening over which the poles 16 and a portion of the connecting strips 50 are suspended. The opening forms part of a pathway for ions traveling through the device, as

described more fully below. The ion filter 29 may be supported on either side of the common substrate, the side facing of the ion source 28 or the side facing the ion detector 32.

The ion filter 29 of the present invention may be incorporated into a quadrupole mass spectrometer in any convenient way. One preferred configuration is shown in FIG. 4, which is an exploded perspective view showing components of one embodiment of a miniature micromachined quadrupole mass spectrometer 10. As shown in FIG. 4, the quadrupole mass spectrometer 10 includes the ion source 28, the ion filter 29 and the ion detector 32. The mass spectrometer 10 also includes an entrance device 12, such as an entrance plate, for controlling the movement of ions in the ion beam 22 into the ion filter 29 and an exit device 14, such as an exit plate, for controlling the movement of the mass filtered ions 30 from the ion filter 20. The mass spectrometer 10 also includes an entrance spacer 18, and an exit spacer 20. During operation of the mass spectrometer 10, the entrance device 12 receives ions in the ion beam 22 from the ion source 28. Ions in the ion beam 22 pass through entrance apertures 24 extending through the entrance device 12 to channel ions into quadrupole channels 17 (as shown in FIG. 2) within the array of electrically conductive poles 16. The exit device 14 is located at a distal end from the entrance device 12 and provides ions with egress through exit apertures 26 extending through the exit device 14. The mass-filtered ions 30 pass to the ion detector 32 for detection.

The array of poles 16 of the ion filter 29 is located adjacent to and between the entrance device 12 and the exit device 14. The entrance spacer 18 maintains a predetermined spacing between the array of poles 16 and the entrance device 12. The exit spacer 20 maintains a predetermined spacing between the array of poles 16 and the exit device 14. The exit spacer 20 also acts as a common supporting substrate for the patterned layer of the ion filter 29. One or both of the spacers 18, 20 may be bonded to the structure of the ion filter 29 and to the entrance and exit devices 12, 14, respectively. As may be appreciated, many bonding methods, preferably non-contaminating bonding methods, such as diffusion- and anodic-bonding techniques, may be employed to obtain good bonding results. The spacers 18, 20 may have any convenient thickness, but typically each have a thickness of smaller than about 1 millimeter and preferably smaller than about 0.5 millimeter.

Referring now to FIG. 5, a partial cross-section is shown through a single opposing pair of the metallic poles 16 for the mass spectrometer 10, except that the ion source 28 and the ion detector 32 are not shown. As with the other figures, the cross-section of FIG. 5 is not necessarily to scale and is shown only for purposes of illustration. Shown in FIG. 5 are the entrance device 12, including one of the apertures 24, the exit device 14, including one of the apertures 26, two directly opposing poles 16, the entrance spacers 18, and the exit spacer 20. Low dielectric-constant materials are preferably used for the spacers 18, 20 to lower capacitance.

With reference to FIGS. 4 and 5, the poles 16 are preferably non-magnetic, non-reactive, metallic rods, such as gold or titanium. The spacers 18, 20 are insulators, preferably of glass, to isolate the poles 16 during operation of the quadrupole mass spectrometer 10 of the present invention.

The entrance device 12 is important to at least partially isolate the ion filter 29 and the ion source 28 and to channel ions from the ion source into the ion filter 29. By acting as an isolation shield, the entrance device 12 reduces the

possibility of detrimental interference between the ion source 28 and the ion filter 29.

The exit device 14 is important to at least partially isolate the ion filter 29 and the ion detector 32 and to channel ions from the ion filter 29 to the ion detector 32. By acting as an isolation shield, the exit device 12 reduces the possibility of detrimental interference between the ion filter 29 and the ion detector 32.

The entrance and exit devices 12, 14 may each be comprised of substantially entirely only dielectric material. As shown in FIG. 5, however, it is preferred that the entrance device 12 and exit device 14 each include a dielectric interior body portion 34, such as a silicon substrate 34, coated with an electrically conductive outer layer 36, preferably a gold/chromium film layer attached to and supported by the body portion 34. Preferably, the electrically conductive outer layer 36 extends into the interior of the apertures 24, 26, as shown in FIG. 5. The electrically conductive outer layer 36 at least partially protects the array of poles 16 during operation of the quadrupole mass spectrometer 10 by dissipating the charge of ions that strike the outer layer 36. The entrance device 12 may have a flat or concave surface for receiving the ion beam 22, and the exit device 14 may have a flat or concave surface for directing the exiting mass-filtered ions 30. As shown in FIGS. 4 and 5, the surfaces are concave. Furthermore, although it is most preferred that the electrically conductive outer layers 36 completely surround the entrance device 12 and exit device 14, as shown in FIG. 5, such complete surrounding is not required. Preferably, however, the conductive outer layer 36 of the entrance device 12 covers at least a portion of, and more preferably substantially all of, the surface of the entrance device 12 facing the ion source 28. Likewise, it is preferred that the conductive layer 32 of the exit device 14 cover at least a portion of, and more preferably substantially all of, the surface of the exit device 14 facing the ion filter 29.

The ion detector 32 is preferably any suitable detector for detecting selected ions of the ion beam 22 in accordance with the invention, such as a Faraday-type ion detector or a single-particle multiplier detector.

With reference primarily to FIG. 4, the ion filter 29 is shown, including the poles 16. The area 52 shown in FIG. 4 is that portion of the ion filter 29 shown in larger scale in FIG. 2. The connecting strips 50 radiate outward from the poles 16 and terminate in electrical connection with one of either bonding pads 44 or bonding pads 46. One of the bonding pads (either 44 or 46), the associated connecting strip 50 and the associated pole 16 are typically manufactured as an integral unit, as described more fully below with the discussion concerning preferred manufacturing methods for making the ion filter 29. Also, the bonding pads 44 and the bonding pads 46 are offset, so that electrical connections may more easily be made to the bonding pads 46 are offset, so that electrical the mass spectrometer 10, an RF frequency voltage and a DC voltage, as described previously, are applied to the poles 16 via electrical connections made to the bonding pads 44, 46. The specific frequency and magnitude of the RF voltage and the specific magnitude of the DC voltage applied to the poles 16 determine the value of  $m/z$  for ions passing through the ion filter 29 to exit with the mass filtered ions 30 for detection. By varying the frequency and/or voltages, the selected  $m/z$  for ions passing through the ion filter 29 may be varied. By continuously or periodically varying the RF frequency and voltages over a predetermined range, the mass spectrometer 10 may be used to scan for ions over a wide range of  $m/z$  values. The mass

spectrometer **10** may be designed for  $m/z$  detection in the range of  $m/z$  of from about 1 to about 4000. For many applications, however, the range for  $m/z$  detection with the mass spectrometer **10** is from an  $m/z$  of about 1 to an  $m/z$  of about 300.

With continued reference to FIG. 4, the patterned layer of the ion filter is substantially entirely supported by the exit spacer **20**, which acts as a common supporting substrate. The exit spacer **20** has an opening **35** through the exit spacer **20**. As the ion filter **29** is supported by the exit spacer **20**, the opening **35** and the ion filter **29** are aligned so that at least the area **52** of the ion filter, including the poles **16** and portions of the connecting strips **50**, are positioned over the opening **35**. Therefore, the poles **16** and at least a portion of the connecting strips **50** are suspended from the exit spacer **20** over the opening **35**. The opening **35** forms part of a pathway permitting ions from the ion source **28** to travel through the ion filter **29** to the ion detector **32**. This pathway includes an entrance aperture **24** through the entrance device **12**, an opening **37** through the entrance spacer **18**, the quadrupole channels **17** (shown in FIG. 2) through the array of the poles **16**, the opening **35** through the exit spacer **20** and the exit apertures **26** through the exit device **14**.

It will be recognized that the relationship between the poles **16** and a common supporting substrate may involve different geometries in the mass spectrometer **10** without departing from the spirit of the invention. For example, the common supporting substrate could include a plurality of openings, rather than just one opening, with a different group of the poles **16** suspended over each of the plurality of openings. Also, the common supporting substrate could be used as an entrance spacer, rather than an exit spacer, with the ion filter supported on the side facing away from the ion source **29**, rather than toward the ion spacer **29**, as shown in FIGS. 4 and 5, and an exit spacer could thus be used that is of similar design to the entrance spacer **18** as shown in FIGS. 4 and 5.

The mass spectrometer **10** may be operated at any convenient RF frequency. Typically, however, the length of the poles **16** (shown as the dimension  $L_p$  in FIG. 5) will be short enough to permit operation of the quadrupole mass spectrometer at low RF frequencies, such as frequencies less than about 50 MHz, which is generally preferred. This lower operational frequency allows the voltage  $V_0$  and  $U_0$  to be maintained at conveniently low values for the desired mass range to reduce the possibility of arcing across closely-spaced parts and to minimize power consumption in the electronics and radiation (varying as the sixth power of frequency). For example, a convenient length,  $L_p$ , of the points **16** may range from about 2 mm to about 6 mm, as previously discussed, and may even be selected to be shorter than about 2 mm.

The use of the short poles **16** and a Faraday-type ion detector allows operation at higher pressures, often in the millitorr range, wherein the particle's mean free path length may be comparable to instrument dimensions. As will be appreciated, operation at higher pressures allows the use of a smaller, less expensive backing pump to create the required vacuum conditions, rather than using, for example, a larger, higher-speed turbomolecular pump in combination with a backing pump.

The entrance device **12**, spacers **18** and **20**, bonding pads **44** and **46**, and exit device **14** may have electrically conductive surfaces since they are located near charged-particle beams to produce known and fixed particle energies. As will be appreciated, the materials used to fabricate all the com-

ponents preferably have coefficients of thermal expansion that are low enough to control distortion caused by operational temperature variations.

As noted previously, the poles **16** may have a hyperbolic shape (to follow the original Mathieu-equation formulation of the quadrupole problem). However, the poles **16** may also have other shapes with negligible loss in mass resolution, such as cylindrical (i.e., with a semicircle or other circle arc sections at the terminal ends forming the poles **16**). Other shapes may provide easier final fabrication of plating molds (discussed below) for the poles **16** and, possibly, a denser packing of the poles **16**.

During operation of the mass spectrometer **10**, of a configuration as shown in FIG. 4, portions of the incident ion beam **22** passes through the entrance apertures **24** contained within the entrance device **12**. Each of the entrance apertures **24** should correspond to and be aligned with one of the quadrupole channels **17** (shown in FIG. 2) within the array of poles **16**, so that the entrance apertures **24** channel ions from the ion source **28** to the ion filter **29**. Ions from the ion beam **22** that pass through the apertures **24** then travel through the array of the poles **16** of the ion filter **29**. Ions exiting the ion filter **29** then depart through the exit apertures **26** contained within the exit device **14** as the mass-filtered ions **30** to be detected by the ion detector **32**. Each of the exit apertures **26** should correspond to and be aligned with one of the quadrupole channels **17** (shown in FIG. 2) within the array of poles **16**, so that the entrance apertures **24** channel ions exiting the ion filter **29** to the ion detector **32**.

Detection sensitivity lost in miniaturization may be at least partially overcome by the use of numerous quadrupoles working in parallel as shown in FIGS. 4 and 5. As will be appreciated, miniaturization tends to reduce detection sensitivity because fewer particles can be admitted into the reduced entrance apertures **24** of the mass spectrometer **10**. Thus, the basic pattern, described above and shown in FIGS. 2-5, can be repeated 1 to 10,000 times or more (depending on the desired results) to form a desired array of poles **16**. Moreover, the poles **16** may be wired to all work in parallel, or different parts of the array of the poles **16** can be tuned to different mass ranges. As will be appreciated, variable control over operations of the spectrometer **10** may be useful when monitoring, for example, in an atmosphere or plasma, a transient phenomena, or a spatially-variable phenomena.

Referring now primarily to FIGS. 4, 6 and 7, a preferred manner for making electrical connections to the poles will now be described. FIG. 6 illustrates a perspective view of one type of bonding configuration and FIG. 7 shows a single quadrupole device for illustrating bonding configuration and FIG. 7 shows a single quadrupole device for illustrating bonding configurations and electrical connections. The metal connecting strips **50** are attached between the bonding pads **44**, **46** and the poles **16** to support the poles **16** of the ion filter **29** suspended over the opening **35** through the exit spacer **20** and to electrically connect the poles **16** to an RF generator (now shown). The bonding pads **44**, **46** are each at a terminal end of the integral piece opposite the poles **16**. The bonding pads **44**, **46** provide additional structural strength for each connected pole **16** and for providing a site for wire bonding at the top of these structures as a secondary method of electrical connectivity.

As shown in FIGS. 6 and 7, the array of the present invention may have parallel wiring in an easy-access configuration. For example, dual tracks, a Track A **40** and a Track B **42**, may be used with the dual bonding pads **44**, **46** (one for each track) and the metal connecting strips **50** to

electrically connect the bonding pads 44, 46 with the poles 16. The metal connecting strips 50 are connected to alternate positive (+) and negative (-) poles 16 of the quadrupole array. Outer metal Track A 40 and inner Track B 42 provide parallel access to the positive (+) and negative (-) poles 16, and all the negative (-) poles 16 may be connected to Track B 42, or vice versa.

The dual bonding pads 44, 46, one for Track A 40 and one for Track B 42, have a sufficient bonding surface, such as approximately 1 mm by 3 mm. The bonding pad of Track A 40 is preferably at least approximately 0.5 mm from Track B 42 so that there is sufficient clearance between Track A 40 and Track B 42. Electrical connectivity is realized by wire bonding, pressure contacting, or electroplating the structure from a previously-patterned substrate, such as exit spacer 20 of FIG. 4. The conducting poles 16, the connecting strips 50 and the bonding pads 44, 46, along with the dual tracks 40, 42 form the ion filter 20 for this embodiment. The exit spacer 20 (as shown in FIG. 4) preferably includes an electrically conductive bonding pattern 33, which is a patterned electrically conductive film that has a pattern that matches and corresponds with the pattern of the connecting strips 50 and the bonding pads 44, 46. The bonding pattern 33 enhances the ability to securely bond the ion filter 29 to the exit spacer 20. Furthermore, bonding of the connecting strips 50 and bonding pads 44, 46 securely to the exit spacer 20 maintains the poles 16 with the desired orientation with the poles suspended over the opening 35.

The present invention recognizes that several fabrication methods may be employed to produce the ion filter 29 of the present invention. It is important, however, that the manufacture method be such that the poles 16, as manufactured, have alignment and relative positioning for final use in a quadrupole mass spectrometer. This is typically accomplished by forming the patterned layer of the ion filter 29 so that it is all substantially supporting by a common supporting substrate, such as the exit spacer 20.

One such method of the present invention for making the ion filter 20 quadrupole array includes the simultaneous fabrication of the poles 16, such as by simultaneously forming the poles 16, and typically also simultaneously forming the remainder of the patterned layer of the ion filter 29, in a mold by filling the pattern of the mold with electrically conductive material. In a preferred embodiment, the mold includes the pattern for all of the poles 16, the connecting strips 50 and the bonding pads 44, 46, which are all then fabricated simultaneously by filling the mold. As may be appreciated, the mold may be produced in a separate process or included as step(s) in making the ion filter 29 of the present invention. Although other methods may be acceptable, one preferred means of creating the mold is through Lithographie-Galvanoformung-Abformung (LIGA) manufacture, discussed in more detail below. Similarly, any acceptable method may be used to fill the mold with electrically conductive material, such as, for example, by electroplating, chemical vapor deposition, physical vapor deposition, or loading voids in the mold with nanoparticles of the desired material. LIGA manufacture is particularly useful for poles 16 having lengths in a range of from about 0.5 mm to about 6 mm, and preferably of from about 0.5 mm to about 4 mm.

Another method of making the array of the poles 16 involves precise selective removal of portions of a work piece, that is initially a single solid sheet of electrically conductive material, to obtain the desired patterned layer for the ion filter 29. It is preferred that all of the poles 16, the connecting strips 50 and the bonding pads 44, 46 be manu-

factured from the same work piece and that the final patterning be done only when the single work piece is supported by a common substrate, such as the exit spacer 20. The selective removal may be any suitable technique. In this regard, Electrical Discharge Machining (EDM), discussed in detail below, may be employed to selectively remove material from the work piece and thereby obtain acceptable tolerances for poles 16. EDM manufacture is particularly preferred for manufacturing poles having a length of at least about 4 mm.

As will be appreciated, the use of the LIGA and EDM fabrication methods facilitates the production of poles 16 of a quadrupole array having the desired relative positioning of the poles 16 in a high density array. In this regard, the density and small size of the array is advantageously achieved by forming all of the poles 16 so that, as manufactured, the patterned layer, including the poles 16, the connecting strips 50 and the bonding pads 44, 46, is supported by a single substrate (e.g., the exit spacer 20). It should, however, be recognized that, although it is preferred that the method of the invention may be used to fabricate the entire patterned layer of an ion filter 29, the invention is not so limited. The method could be used, for example, to manufacture only an array of poles 16 in alignment, with electrical connections to the poles 16 being made other than through the connecting strips 50 and bonding pads 44, 46.

With EDM-based manufacture, all of the poles 16 and other portions of the patterned layer of the ion filter 29 are formed by selective removal of material from a single piece of electrically conductive material that has been first bonded to and supported on a common substrate (e.g., exit spacer 20) so that the patterned layer of the ion filter 29 will be supported by the common supporting substrate. In this manner, proper alignment of the poles 16 is established concurrently with manufacture of the poles 16. By manufacturing the poles 16 so that, as manufactured, they are supported by a common supporting substrate, problems associated with positioning and aligning preformed rods, as is encountered with manufacture of conventional quadrupole devices, may be avoided. Rather, with the present invention, positioning and alignment of the poles 16 are accomplished during the same process operation in which the poles 16 are formed, considerably simplifying manufacture of the ion filter 29 by eliminating steps involving positioning and aligning loose, preformed rods.

#### METHOD OF FABRICATION USING A MOLD

The manufacturing method of the present invention will now be exemplified with a description of one embodiment of the method involving formation of an array of poles, and other portions of the patterned layer of the ion filter, by filling a mold. Preparation of the mold by the LIGA technique is also described, although it will be appreciated that the mold could be made by any suitable technique or could be acquired from an external source, such as an outside specialty manufacturer. FIG. 8 shows a process flow diagram illustrating one embodiment of the LIGA-based fabrication process of the present invention. It will be appreciated that the order of the steps is intended to be only illustrative in nature.

The LIGA method is employed in the present invention to manufacture a mold, which is also sometimes also referred to as a template. The mold may be made of any suitable material, but is typically a polymeric material, such as polymethyl methacrylate (PMMA) or a polyimide. A preferred material for the mold is PMMA. The discussion here

will, therefore, be with reference to PMMA as an example of the mold material. The same principles apply to other mold materials. The molds are filled with an electrically conductive material to form the patterned layer of the ion filter, including an array of the poles. Because electroplating is a preferred method for filling the molds, the process is discussed with reference to electroplating by way of example. The same principles apply, however, to other methods for filling the mold.

To manufacture a quadrupole mass spectrometer with the ion filter, other components such as entrance and exit devices and spacers are manufactured and then modularly assembled with the ion filter. The resulting quadrupole mass spectrometer is typically  $\frac{1}{50}$ th, or smaller, of the mass and volume of present commercial quadrupole mass spectrometer devices. In that regard, the quadrupole mass spectrometer 10, as shown in FIGS. 4 and 5, may have a weight of smaller than about 7 grams and may occupy a total volume of smaller than about 2 cubic centimeters. Detection sensitivity lost in miniaturization may be at least partially overcome by fabricating the ion filter with a plurality of quadrupoles working in parallel, thereby increasing the area available for ion travel. For example, the ion filter of the present invention could include 10,100 or even 10,000 or more quadrupoles. Although it will be appreciated that as the number of quadrupoles becomes very large, the size of the device will necessarily increase.

Using LIGA-based techniques, fabrication of the patterned layer of the ion filter is accomplished, for example, through electron-beam lithography (to manufacture repetitive gold LIGA X-ray masks using intermediate steps of contact-printing and gold-plating) followed by X-ray exposure of the PMMA in a synchrotron light source. The exposed PMMA is chemically developed away, the pattern of void spaces are filled by electroplating with electrically conductive material (gold or titanium is preferred), and exit and entrance spacers and entrance and exit devices having apertures are provided for assembly. After these components are aligned, assembled, and bonded together, an RF generator may be connected (e.g., through wire bonding techniques) and an ion source and ion detector provided to complete fabrication of a mass spectrometer.

LIGA-based processing is suitable to this manufacture because it is capable of producing high dimensional accuracy which allows the quadrupole array (e.g., poles) to be electroplated to a close tolerance, preferably to within a 0.1% dimensional tolerance. The LIGA method achieves this accuracy at least in part by using computer-aided mask manufacture to create masks used in fabricating the final template. To further improve the quality of the produced quadrupole array, advanced bonding techniques, such as anodic, diffusion, eutectic, or ultrasonic bonding, can be used to create contamination-free, corrosion- and temperature-resistant bonds without altering the dimensions of poles, connecting strips, and bonding pads.

#### One Embodiment of LIGA-Based Fabrication:

With reference to FIG. 8 showing the sequence of processing steps and FIG. 4 showing various components of the quadrupole mass spectrometer 10, one embodiment of LIGA-based fabrication of the patterned layer of the ion filter 29 is described.

#### (a) Fabricate Optical Mask:

In this step, an optical photomask is fabricated for subsequent use in the fabrication of an X-ray mask. A standard electron-beam lithography apparatus is used to etch the "footprint" or pattern of the ion filter (i.e., poles 16, con-

necting strips 50, and bonding pads 44, 46) in a resist material coating a quartz-substrate on which a UV opaque material, typically chromium, has been previously deposited. In this regard, the electron beam can be precisely controlled to an accuracy of about 1 nm in 1 cm. After exposure to the electron beam, the undesired resist material is developed away, and the entire mask is then placed in an etchant bath to remove the chromium film from the exposed areas. The remaining resist is then removed leaving the previously-protected chromium pattern to be used as an optical mask for further lithography.

#### (b) Fabricate X-Ray Mask:

The optical mask of step (a) is next used to fabricate an X-ray mask (to be used in the subsequent exposures in the synchrotron light source, see (c) below). The optical mask of step (a) is laid over a plate consisting of a 50 micron layer of photoresist coated over a 300 angstrom layer of gold, itself on a 50 angstrom layer of chromium, all supported on a silicon substrate. The assembly is then exposed to collimated ultraviolet (UV) radiation which replicates the pattern of (a) by passing through the quartz-only portions of the optical mask. Next, the undesired photoresist is developed away, and gold is then plated into these developed regions. As can be appreciated, this process creates a four-layer mask consisting of a patterned 50 micron gold layer on a 300 angstrom gold layer, itself on a 50 angstrom chromium layer, all on the silicon substrate.

#### (c) Expose PMMA Through X-Ray Mask:

A PMMA sheet, having a thickness slightly greater than the final desired thickness of the patterned layer of the ion filter 29 is then exposed through the X-ray mask of step (b) to synchrotron X-ray radiation. The excess thickness is provided to accommodate lapping of the final structure, as discussed below. A synchrotron light source is used because it provides a collimated, intense beam of X-rays. These X-rays irradiate the PMMA sheet through the X-ray mask at the thin-gold locations. Because the X-rays are blocked by the thick-gold areas of the mask, the pattern of the ion filter is replicated in the PMMA sheet. A single X-ray mask may be used to pattern numerous PMMA sheets.

#### (d) Develop Exposed PMMA:

The PMMA sheet of step (c) is then placed in a suitable mixture of solvents, such as methyl isobutyl ketone (MIBK), to dissolve the portion of the PMMA sheet exposed to X-rays in step (c). The solvent mixture is chosen so as not to dissolve or otherwise deteriorate portions of the PMMA sheet not exposed to X-rays. The resulting patterned PMMA sheet provides a template of the ion filter than can now be used as a mold that can be filled with electrically conductive material to form the patterned layer of the ion filter 29, including the array of the poles 16 for the quadrupole array of the present invention. The process up to this point has been involved with making the mold. It should be recognized, however, that the mold could be made by any suitable technique or could be purchases in a premanufactured state from an outside source.

#### (e) Fill PMMA Mold:

Using standard electroplating methods, the PMMA mold of step (d) may now be filled with a selected electrically conductive material (e.g., gold or titanium) to form the quadrupole array. To facilitate electroplating and further fabrication of the quadrupole mass spectrometer of the present invention, the PMMA mold may be placed on a electrically conductive base on a common supporting substrate (e.g., bonding pattern 33 on exit spacer 20) that will form part of the finally assembled mass spectrometer.

17

Because the exit spacer **20** is preferably fabricated from a electrically non-conductive material (e.g., ceramic or other dielectric), the electrically conductive bonding pattern **33** is bonded to the exit spacer **20** prior to placing the PMMA mold on the exit spacer **20**, typically by standard thin film or thick film deposition techniques. It will be appreciated that at this point in the manufacture process, the exit spacer **20** will not include the opening **35**, so that there will be a solid surface to electroplate against in the area that the opening **35** will eventually occupy.

A typical way to provide the bonding pattern **33** on the exit spacer **20** is to initially deposit a continuous film of electrically conductive material (e.g., gold) on the surface of the exit spacer **20** (i.e., the ceramic material is metallized). The pattern of the ion filter **29** is then lithographically imprinted in this electrically conductive film and the exit spacer **20**, with the lithographically imprinted film, is placed in an etchant bath to selectively remove the electrically conductive film from the exposed areas, thereby forming the electrically conductive bonding pattern **33**. In this manner, the bonding pattern **33** is produced on, and bonded to, exit spacer **20**. The PMMA mold is now located on the exit spacer **20** so that the bonding pattern **33** is aligned with the pattern for the ion filter **29** in the PMMA mold. The PMMA mold is filled with the appropriate electrically conductive material (e.g., gold or titanium) by electroplating to the bonding pattern **33** that is exposed through the PMMA mold. The final electroplated structure is lapped (e.g., abrasive lapping with a fine-diameter slurry) to provide a flat planar surface having a desired surface finish for subsequent processing and to establish the desired final thickness of the patterned layer of the ion filter **29**, which is equal to the desired final length of the poles **16**.

(f) Dissolve PMMA Mold:

After the filled PMMA mold has been lapped, the remaining PMMA of the mold is then dissolved in a solvent, such as methylene chloride, leaving a free-standing structure of the ion filter **29** (including the array of poles **16**, the connecting strips **50** and the bonding pads **44**, **46**) bonded to the corresponding bonding pattern **33** and supported by the exit spacer **20**. Also, as will be appreciated, the mold may be removed by techniques other than dissolution in a solvent. For example, the material of the mold could be removed by laser ablation. The exit spacer **20** may be machined to create the opening **35** before or after the mold is removed. As will be appreciated, the opening **35** may be produced by employing various machining methods. A preferred technique is ultrasonic machining. For example, ultrasonic impact drilling may be used which involves placing an abrasive slurry in contact with exit spacer **20** and then using a tool, having the shape of the desired opening **35**, to rapidly (e.g., reciprocating vibrations at 15 to 30 kHz or higher) and forcefully agitate the fine abrasive materials in the slurry, thereby removing material of the exit spacer **20** to form the opening **35**.

The ion filter **29** may now be assembled with other components to make the quadrupole mass spectrometer **10**. For example, the entrance spacer **18**, typically of glass, may be placed on the exposed-and-lapped surface of the ion filter **29**, and the entrance device **12** then placed above the entrance spacer **18**. The exit device **14** may then be bonded or clamped to the underside of the exit spacer **20**. As will be appreciated, alignment of the components may be facilitated through the use of fiducial marks. The entire assembly may then be bonded in place using methods including, for example, the use of adhesives (of low vapor pressure, so as not to cause contamination), anodic bonding, thermal com-

18

pression bonding, diffusion bonding, glass-to-metal seals, gold eutectic solder, or constraining the assembly in place through non-deforming mechanical clamping. The ion source **28** may then be coupled to the entrance device **12**, and the ion detector **32** connected to the exit device **14**, and an RF generator may be connected to the bonding pads **44**, **46** to make the device functional.

It should be recognized that in the broadest sense, the manufacture method of the present invention involving the use of a mold to form the pattern of the poles **16** need not include all of the steps described with reference to FIG. **8**. Rather, it is sufficient that a mold be used to form the pattern so that the poles **16**, as they are formed in the mold, have relative positioning and alignment for use in a quadrupole mass spectrometer.

#### METHOD OF FABRICATION USING EDM TECHNIQUES

FIG. **9** shows a process flow diagram illustrating one embodiment of the Electrical Discharge Machining (EDM) based process of the present invention. EDM is a machining process that selectively removes metallic material from a work piece by spark erosion. Unlike conventional machining, which mechanically shears tiny strips from the workpiece, EDM uses alternating current (AC) or direct current (DC) from a special generator to melt and vaporize conductive material away from the workpiece. Cooling and cleaning is usually provided by pumping deionized water through the cutting region. In a preferred embodiment, the present invention includes a small diameter (e.g., 0.001 inch) alloy wire electrode that is driven by machines with accurate computer-controlled drives in the x, y and z axes. The machines are computer programmed to give the desired final geometry and dimensions of the workpiece.

##### One Embodiment of EDM-Based Fabrication:

With reference to FIG. **9** showing the sequence of processing steps and to FIG. **4** showing various components of the quadrupole mass spectrometer **10**, one embodiment of EDM fabrication of the patterned layer of the ion filter **29** is described.

##### (a) Bond Work Piece to Substrate:

A supporting substrate (e.g., exit spacer **20**) is provided having the bonding pattern **33**. To the bonding pattern **33** is bonded a single work piece, in the form of a sheet of electrically conductive metal (e.g., gold or titanium). The sheet preferably has a thickness that is substantially equal to the desired thickness for the final patterned layer of the ion filter **29**, and therefore also substantially equal to the desired final length of the poles **16**. The bonding pattern **33** may have been formed on the exit spacer **20** as previously described in the discussion concerning LIGA-based manufacture. Bonding of the work piece to the bonding pattern **33** on the substrate may be accomplished in any suitable manner. A preferred manner of bonding is by the use of solder placed between the bonding pattern **33** and the work piece. Also, it is preferred that at the time the work piece is bonded to the exit spacer **20**, the exit spacer already has the opening **35** therethrough. It is, however, possible to make the opening **35** after the work piece has been bonded to the exit spacer **20**, if desired. Also, the opening **35** may be made before or after the bonding pattern **33** has been formed on the exit spacer **20**.

##### (b) Pattern Work Piece:

After the work piece has been bonded to the substrate, wire EDM is used to selectively remove material from the work piece to form the patterned layer of the ion filter **29**,



including the poles 16, connecting strips 50 and bonding pads 44 and 46. The geometry and accuracy of the selections removed are controlled by the software and accurate x, y, and z directional drives and is preferably to within a 0.1% dimensional tolerance. As will be appreciated, the metallic work piece may have been at least partially patterned (through EDM or other methods) prior to being bonded in step (a) to the bonding surface on exit spacer 20. For example, the bonding pads 44 and 46 and the connecting strips 50 may be at least partially patterned prior to bonding to the exit spacer 20, simplifying the patterning of the work piece on the substrate. It is important, however, that the final division of the work piece into the separate integral pieces for each of the poles 16 not occur until after the work piece has been bonded to the exit spacer 20. In this way, the poles 16 are formed with the proper positioning and alignment for use in a quadrupole mass spectrometer, with the positioning and alignment being retained by the bond to the exit spacer 20.

It should be appreciated that in its broadest sense, the EDM processing of the present invention does not require the first step shown in FIG. 9, i.e., the bonding step. The substrate could be acquired from an outside supplier with the work piece already bonded to the substrate. It is sufficient that selective removal of material from the work piece bonded to the substrate occur in a manner such that the poles 16, as they are formed, have the relative positioning and alignment for use in a quadrupole mass spectrometer.

After the work piece has been patterned into the patterned layer of the ion filter 29, then the ion filter 29 may be assembled, along with other components, into the mass spectrometer 10, in a manner as previously described.

APPLICATIONS

As will be appreciated, the use of the above discussed LIGA-based and EDM-based fabrication processes facilitate the production of accurate, miniature quadrupole mass spectrometers with reduced complexity of manufacture relative to conventional manufacture of quadrupole mass spectrometers. It is anticipated that the reduced cost and advantageous size of the quadrupole mass spectrometer of the present invention will have many commercial applications. In this regard, the miniature quadrupole mass spectrometer of the present invention may be used for process control, personnel safety, and pollution monitoring. Also, the small size of the present invention allows small sensors containing the miniature quadrupole mass spectrometer to be manufactured. Commercial applications of the small sensors may include distributing the sensors throughout the manufacturing plants, in public areas (such as buildings and subway systems), within plasma chambers (chip manufacturers), in earth-orbiting space stations, in long-duration human flight missions, for planetary aeronomy and planetary-surface studies, etc. Other commercial applications of the present invention may include automotive exhaust monitoring, home fire/radon/CO monitoring, personnel environmental monitoring, smokestack monitoring, and down-hole monitoring.

Also, because of the small size of the device, a high vacuum may not be required in some applications. This is because the requirement of small particle mean free path relative to the (small) spacing of the poles, as described above, can now be met with the present invention at a higher ambient pressure. This obviates the need for sophisticated pumping and can place devices of the present invention into the realm of operation of, for example, micromachined

peristaltic pumps. Use at the higher pressures would require a pressure-resistant electron emitter (such as a filed ionizer) to ionize the neutral species and a Faraday cup as the ion detector.

Furthermore, although the present invention has been described primarily in reference to the quadrupole mass spectrometer, the invention, in its broadest aspects is not so limited. Rather, one important aspect of the present invention relates to the ion filter described herein and methods for making the ion filter.

Moreover, while the invention has been described in combination with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Specifically, it should be understood that the order of the fabrication and assembly of the present invention may be altered from that given as an illustration. Further, it should be understood that a fabrication step may be omitted (e.g., by purchasing a prefabricated component) and still be within the spirit of the present invention. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

What is claimed is:

- 1. A method of mass-filtering an ion beam, the method comprising:
  - receiving the ion beam through an entrance device with at least one entrance aperture;
  - filtering said ion beam with a patterned layer of electrically conductive material, said patterned layer including a plurality of elongated electrically conducting portions, each portion including, in a single integral piece, a pole and a bonding pad, where said filtering includes passing said ion beam through a channel formed by an array of poles;
  - exiting said ion beam as mass-filtered ions through an exit device located at a distal end from the entrance device and having at least one exit aperture; and
  - receiving the mass-filtered ions by a detector.
- 2. The method of claim 1, wherein:
  - the entrance device is a plate with a concave surface for receiving the ion beam; and
  - the exit device is a plate with a concave surface for exiting the ion beam.
- 3. The method of claim 1, wherein the entrance and the exit devices are gold plates comprises of a silicon substrate coated with a gold/chromium film outer layer.
- 4. The method of claim 1, wherein the entrance and exit devices are titanium plates.
- 5. The method of claim 1, wherein the pole of said each portion includes at least one curved exterior surface.
- 6. The method of claim 5, wherein the channel and said at least one curved exterior surface form a hyperbolic shape.
- 7. A miniature quadrupole mass spectrometer array for analyzing an ion beam, comprising:
  - a plurality of micromachined entrance apertures for receiving the ion beam and a plurality of micromachined exit apertures located at a distal end from the entrance apertures and for providing said ion beam with egress as mass-filtered ions;
  - an ion filter adapted to be located between the entrance aperture and the exit aperture to mass filter ions, said ion filter including a patterned layer of electrically conductive material, said patterned layer including a plurality of elongated electrically conducting portions,



21

each portion including, in a single integral piece, a pole and a bonding pad, where poles from said plurality of conducting portions are arranged into an array of poles to define a space between the poles as a channel for passing the ions; and  
a detector located adjacent the exit aperture for receiving the mass-filtered ions.

8. The array claim 7, wherein a group of four adjacent poles in said array of poles comprises a quadrupole, said quadrupole defining the channel through which ion travel to be filtered.

9. The array of claim 7, wherein the pole of said each portion has a length of shorter than about 6 millimeters.

10. The array of claim 9, wherein the patterned layer has a substantially constant layer thickness, which is substantially equal to the length of the pole of said each portion.

11. The array of claim 7, further comprising:  
a plurality of connecting strips, each of said connecting strips configured to act as an electrical lead from the bonding pad to the pole, such that said pole, said plurality of connecting strips and said bonding pad for a single integral piece.

12. The array of claim 11, wherein said each of said connecting strips has a width smaller than about 0.5 millimeter.

22

13. The array of claim 7, wherein the pole of said each portion includes at least one curved exterior surface.

14. The array of claim 13, wherein the channel and said at least one curved exterior surface form a hyperbolic shape.

15. The array of claim 7, wherein terminal portions of the pole of said each portion forms a semicircle.

16. The array of claim 15, wherein a cross sectional area of the semicircle is smaller than about 0.3 square millimeter.

17. The array of claim 7, wherein a group of four adjacent poles in said array of poles comprises a quadrupole, said quadrupole defining the channel through which ions travel.

18. The array of claim 17, wherein a face-to-face spacing between adjacent, directly opposing poles in said quadrupole is smaller than about 0.2 millimeter.

19. The array of claim 17, wherein a spacing between diagonally opposing poles in said quadrupole is smaller than about 0.3 millimeter.

20. The array of claim 17, wherein said ion filter is configured such that said ion filter includes at least two quadrupoles per square millimeter.

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